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Original Article

Surface characterization of nickel titanium orthodontic arch wires

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ARTICLE INFO

Article history:

Received 13 September 2013

Accepted 11 December 2013

Available online 3 April 2014

Keywords:

Nickel titanium arch wire

Root mean square roughness

Scanning electron microscopy

Raman spectroscopy

Atomic force microscopy

3D profilometry

ABSTRACT

Background: Surface roughness of nickel titanium orthodontic arch wires poses several clinical challenges. Surface modification with aesthetic/metallic/non metallic materials is therefore a recent innovation, with clinical efficacy yet to be comprehensively evaluated. **Methods:** One conventional and five types of surface modified nickel titanium arch wires were surface characterized with scanning electron microscopy, energy dispersive analysis, Raman spectroscopy, Atomic force microscopy and 3D profilometry. Root mean square roughness values were analyzed by one way analysis of variance and post hoc Duncan's multiple range tests.

Results: Study groups demonstrated considerable reduction in roughness values from conventional in a material specific pattern: Group I; conventional (578.56 nm) > Group V; Teflon (365.33 nm) > Group III; nitride (301.51 nm) > Group VI (i); rhodium (290.64 nm) > Group VI (ii); silver (252.22 nm) > Group IV; titanium (229.51 nm) > Group II; resin (158.60 nm). It also showed the defects with aesthetic (resin/Teflon) and nitride surfaces and smooth topography achieved with metals; titanium/silver/rhodium.

Conclusions: Resin, Teflon, titanium, silver, rhodium and nitrides were effective in decreasing surface roughness of nickel titanium arch wires albeit; certain flaws. Findings have clinical implications, considering their potential in lessening biofilm adhesion, reducing friction, improving corrosion resistance and preventing nickel leach and allergic reactions.

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<http://dx.doi.org/10.1016/j.mjafi.2013.12.006>

Introduction

Ever since the report of 'shape memory effect' in nickel titanium (NiTi) alloy in 1962, several applications of the material in medical and dental disciplines have been identified till now.¹ Nickel titanium (NiTi) arch wires with its unique shape memory and super elasticity properties are integral components of contemporary orthodontic practice.² However, the high content of nickel (Ni: 47–50%) in NiTi alloys and its extremely rough surface topography are confronting issues in orthodontics.³ The increased propensity of plaque accumulation, frictional forces at wire-bracket interface, nickel leach and wire fracture ensuing intra oral corrosion are consequent to it.⁴ Nickel release, in turn is known to initiate several adverse responses, ranging from allergic hypersensitivity reactions to extremes of carcinogenic changes.⁵ As for any other metallic alloy, NiTi also has oxide layers on its surface (TiO₂, TiO, Ti₂O₅ and NiO), which renders it the natural protection.⁶ These oxides are formed on the wire surface during its 'wire drawing procedures' from large 'ingot' blocks.¹ Yet, these are removed during clinical use and electrochemical potential differences are generated which initiates pitting and crevice corrosion.^{7,8} To a large extent, all these have been attributed to the high surface roughness of NiTi wires.^{9–11}

In this context, there are some attempts to modify NiTi arch wire surface with metals, non-metals and aesthetic materials with the objective of reducing surface roughness so as to enhance esthetics and to lessen friction, corrosion and nickel leach.¹² Surface engineering as a distinct discipline has made remarkable strides in the field of material technology during the last two decades and its medical and dental applications are manifold.^{12–14} Configuring a surface barrier layer on biomaterials like pacemakers, stents, implants and other devices with an 'environment-friendly material' is an innovative step for improving biocompatibility.¹⁵ Surface modification of dental materials are done either through plasma spraying or physical/chemical vapour deposition; where atoms, ions or molecules activated by plasma, laser or high energy beams are condensed on the substrates.^{16,17} The methods specifically used for orthodontic arch wires are electron beam deposition, magnetron sputtering, cathodic arc deposition or pulsed laser deposition.¹⁸

Surface roughness of materials is measured by profilometric or optical methods and is generally expressed as root mean square (RMS) values.¹⁹ Earlier, invasive profilometric procedures were used to determine surface roughness of NiTi wires.²⁰ At present, there are many non invasive options for assessing the exteriors of materials used in industry, medicine and dentistry. These include qualitative and quantitative means like scanning electron microscopy (SEM), energy dispersive analysis (EDS), spectroscopic techniques like Raman spectroscopy, atomic force microscopy (AFM) and of late, the advanced three dimensional optical profilometry (3D OP).²¹ Still, these have not so far been comprehensively used to evaluate the topography of surface modified NiTi wires. In this study, prototypes of all currently available versions of these wires were included to assess the surface features, which have a close bearing on their clinical performance. Additionally, none of these products are indigenously

manufactured and there is an influx of these imported products into Indian dental market at a high cost but with fewer evidences in favour of them.

The aim of the current study was therefore to characterize the topographic features of five newly introduced surface modified NiTi wires along with a conventional type, using advanced optical methods.

Material and methods

The study groups included 5 types of surface modified nickel titanium wires and one group of conventional NiTi in 0.016 inch (0.406 mm) round dimension. Group 1: Conventional NiTi; (Ortho Organizers, San Marcos, CA), Group II: Spectra Epoxy (GAC International, Bohemia, NY), Group III: Neo Sentalloy (GAC International, Bohemia, NY), Group IV: Black Titanium (Class One Orthodontics, St. Lubbock), Group V: Teflon (d-Tech Asia Ltd, Pune) and Group VI: Silver–Rhodium (d-Tech Asia Ltd, Pune). Since group VI had a dual covering of silver and rhodium, they are represented as group VI (i) for silver and group VI (ii) for rhodium. The study design is shown in Table 1.

Preliminary surface analysis of the arch wires were done with SEM (SNE-3000M model, SEC, Korea) at 500× magnification. Elemental mapping was carried out with EDS (SNE-3000M model, SEC, Korea) and Raman Spectroscopy (HR 800, Jobin Yvon, Spectrometer, Horiba Ltd, Minami-Ku, Kyoto) equipped with 1800 grooves/mm holographic grating. Helium–Neon laser of 633 nm was used as the excitation source. The laser spot size of 3 µm diameter was focused on the sample surface using a diffraction limited 10× objective. The laser power at the sample was ≈20 mW and slit width of the monochromator was 400 µm. The back scattered Raman spectra were recorded using super cooled (<–110 °C) 1024 × 256 pixels charge coupled device (CCD) detector with range from 80 cm^{–1} to 2000 cm^{–1} with 5 s exposure time and 20 CCD accumulations. All the spectra were then baseline corrected. Three different areas of the wire were checked for each sample.

Surface roughness was initially evaluated with Solver Pro EC atomic force microscope (NT-MDT, Zelenograd, Moscow). All measurements were carried out in contact mode using a standard conical silicon tip attached to a cantilever having a force constant of 5 nNm^{–1} with a frequency limit from 50 to 150 Hz. The radius of curvature of the tip was 10 nm and the cone angle was <22°. The scan area was 50 × 50 µm of each sample, at three different locations. Averages of these from six (n = 6/group) wire samples were taken to express the

Table 1 – Study design (n = 6 per group) of arch wires in 0.016 inch (0.406 mm) round dimensions.

Group	Product	Manufacturer
I	Conventional NiTi	Ortho Organizers, San Marcos, CA
II	Spectra Epoxy	GAC International, Bohemia, NY
III	Neo Sentalloy	GAC International, Bohemia, NY
IV	Black Titanium	Class One Orthodontics, St. Lubbock
V	Teflon	d-Tech Asia Ltd, Pune
VI	Silver–Rhodium	d-Tech Asia Ltd, Pune

Fig. 1 – Scanning electron micrographs of arch wires at 500× magnification for (a) Group I (sub figures can be viewed online).

surface roughness as RMS value in nanometre, using the proprietary software of the equipment.

Samples were then re-evaluated for RMS values using Wyko NT 1100 series 3D optical profilometer (Veeco instruments, Inc, Woodbury, NY). Here, white light passes through a beam filter which directs the light to the sample surface and a reference mirror. When the light reflected from these two surfaces recombine, a pattern of interference arises and from these, surface roughness is determined. The Wyko vision software used that data to determine the RMS values from the averages of 3 different regions in a sample. Mean values from both AFM and 3D OP were used to find out the final readings.

RMS values were statistically evaluated with analysis of variance (One way ANOVA, $p < 0.05$) along with post hoc comparison and Duncan's Multiple Range (DMR) test to elucidate multiple comparisons among different groups.

Results

Fig. 1 shows the arch wire surfaces using SEM. Conventional NiTi demonstrated a highly irregular surface with striations in the longitudinal axis. It depicted the stripes and markings inflicted on the wire during manufacture. Variations in surface texture with different materials were evident from the

Fig. 2 – Energy dispersive analysis of arch wires; (a) Group I (sub figures can be viewed online).

Fig. 3 – Raman spectra of arch wires; (a) Group I (sub figures can be viewed online).

SEM images. Group II, Spectra Epoxy showed a smooth resin surface but had small holes sparsely distributed on its surface. Nitride ions on group III appeared flaky, crusty and less adherent. Metallic surfaces like titanium, silver and rhodium were homogenous and smooth with only minor breaks. The second aesthetic material Teflon; however, had numerous voids on its surface.

The surface elemental composition of each group are shown in the EDS analysis in **Fig. 2**. Control NiTi showed the main components; nickel and titanium besides trace elements like aluminium, chromium, iron and copper. **Fig. 3** shows surface compositions reconfirmed with Raman spectroscopy. Peaks of the graph corresponded to respective elements on the wire surface and were derived from standard Raman values.

Figs. 4 and **5** show the three dimensional AFM and OP views of arch wires. The RMS values correlated to the qualitative assessment made with SEM. Conventional (control) NiTi had the highest RMS values with 578.56 nm where as resin wires; group II, recorded lowest values of 158.60 nm. The irregularities of the nitride surface were obvious in the AFM and 3D OP. The relatively smooth and continuous surfaces with titanium, silver and rhodium metals as observed in SEM were substantiated with corresponding low RMS values (229.51 nm, 252.22 nm and 290.64 nm respectively). The numerous pores and voids on Teflon layers of group V contributed to a high RMS value (365.33 nm); in relation to other study groups, though still less from the control. Mean surface roughness (RMS) values are illustrated in **Fig. 6** and statistical analysis in **Table 2**.

Fig. 4 – Three dimensional atomic force microscope views of arch wires; (a) Group I (sub figures can be viewed online).

Fig. 5 – Three dimensional profilometry views of arch wires; (a) Group I (sub figures can be viewed online).

Discussion

Surface roughness; usually measured by RMS values, is a fundamental property of an arch wire. AFM and 3D OP, which offer good accuracy in measuring surface roughness, were used in the present investigation. Conventional/control NiTi topped among the study groups in terms of RMS values at 578.56 nm; well within the range (100–1300 nm) reported previously for NiTi.^{21,22} This high roughness is mainly ascribed to the grain re-crystallizations that occur when NiTi wires are pulled through diamond moulds during its fabrication.⁵ The SEM images also depicted an exceedingly rough surface, with areas of 'pickling/pores/white inclusion spots' that are characteristically described for NiTi wires.²¹

EDS determines the elemental composition of a material on interaction with X-rays, depending on the energy differences that occur during excitation and down fall of its electrons.²³ Raman spectroscopy, on the other hand is based on the in-elastic scattering of a monochromatic laser with a material. Frequency of the re-emitted photons from the

Table 2 – One way analysis of variance of mean root mean square (RMS) values for different groups (n = 6 per group and P < 0.001).

Parameter	Group	Mean RMS value in nm	SD
Surface Roughness	I; Conventional NiTi	578.56 ^a	48.68
	II; Spectra Epoxy	158.60 ^b	28.49
	III; Neo Sentalloy	301.51 ^c	19.95
	IV; Black Titanium	229.51 ^d	11.11
	V; Teflon	365.33 ^e	12.65
	VI (i) Silver	252.22 ^f	17.34
	VI (ii) Rhodium	290.64 ^g	10.26

Different superscripts; a, b, c, d, e, f and g indicate that mean values differed significantly from each other for all the groups (Duncan's multiple range test).

material shows a characteristic 'up' or 'down shift' with respect to the original, known as 'Raman Effect'. Raman spectroscopy thereby gives information on the low frequency transitions in molecules and delineates its material composition.²⁴

Surface modification using titanium nitride (TiN) over NiTi alloys have been used in industry for different purposes. But with straight grain boundaries and open porosities, they did not form a homogenous surface; instead, rendered open percolation of reactive agents.¹⁶ At present, finer titanium aluminium nitride (TiAlN) is used for making impervious layers over NiTi alloys. Similar methods are being used for NiTi arch wires also, but exact parameters of temperature and pressure used for surface modification are not known.¹⁷ Nitride ion implanted wires were among the first to be marketed in the surface modified NiTi series.¹⁴ In this study, nitride ion deposited (Group III) showed a low RMS value (301.51 nm), with respect to the control (578.56 nm). However, the surface appeared loose and grossly incongruous in the SEM.

Demand for aesthetic orthodontic appliances is mostly met by transparent ceramic or composite brackets. To match these

Fig. 6 – Mean root mean square (RMS) values of arch wires in nanometre.

brackets, resin/Teflon modified NiTi wires are attempted by atomization procedures. Teflon wires demonstrated roughness values (365.33 nm) less than the control, but were higher than other study groups. It correlated well with the large number of elliptical voids observed in SEM, AFM and 3D OP images, indicative of inadequate surface modification with Teflon. Characteristic to Teflon or poly tetrafluoro ethylene (PTFE) is a fluoridated chain which is responsible for its aesthetic and non adherent nature. Confirming this, EDS and Raman spectra showed predominance of fluoride ions on its surface. Since frictional coefficient of Teflon is low, arch wires with Teflon surface are cited to have reduced resistance to sliding mechanics.²⁵ Another aesthetic material; resin wires (Group II) showed carbon, hydrogen and oxygen peaks in the EDS and Raman spectroscopy. Carbon on NiTi surface is known to form 'nickel-titanium-carbide' or 'titanium carbide' hard layers capable of preventing nickel leach.⁴ Contrary to Teflon; resin NiTi had an extremely smooth topography with the lowest RMS value (158.60 nm). Though less in number than Teflon, resin group also showed few voids on its surface in the SEM and AFM images, suggestive of defects in arch wire modification with aesthetic materials.

Biocompatibility of titanium can be the persuading factor for using it for surface modification over NiTi arch wire. Same is the case with other biocompatible metals like silver and rhodium. However, colour of these metals may not fetch necessary appeal among patients and clinicians. Comparable RMS values, were seen for group IV (titanium; 229.51 nm) and VI which had dual surfaces with rhodium (290.64 nm) on the anterior and silver (252.22 nm) on the posterior spans. This implied that modifying NiTi arch wire surface with metals offer a promising option for reducing roughness. SEM, AFM and 3D OP images proved the uniform topography accomplished with metals.

Irrespective of the metallic structure, orthodontic alloys undergo corrosion of varying degrees due to the effects of pH, temperature, microbes and enzymes. Corrosion causes disintegration of orthodontic appliances, release of constituent elements and deterioration of their mechanical and clinically desirable properties. Orthodontic wires are constantly engaged with brackets using ligatures or modules and therefore make conducive sites for corrosion. Arch wire surface being the main interacting area in this, altering its topography can bring out favourable changes in corrosion features. It is based on the conviction that the high surface roughness of NiTi is a chief causative factor for corrosion.¹¹ Among the several natural oxides on its surface; TiO₂ is the predominant one, which gives inherent protection to NiTi against corrosion. Even this protective layer is disrupted by mechanical, biological and chemical actions in the oral cavity and cause 'hydrogen ion entrapment,' which makes the alloy brittle and susceptible to fracture.^{10,26} Tan and co-workers¹² found that for the NiTi alloy; the 'breakdown potential,' an index of the corrosion resistance, can be increased by ion implantation with oxygen. Similar results were reported by Sawase et al as well giving credence to the view point of modifying NiTi surface for evading corrosion.²⁷

Orthodontic wires containing nickel have been implicated to cause a Type IV delayed hypersensitivity immune response, mediated by the release of nickel ions into the oral cavity. Use

of NiTi arch wires can convert 20% of non sensitive Ni subjects into Ni sensitive subjects where the allergy is manifested as burning papular erythema or papulovesicular dermatitis.¹⁴ Nickel also affects polymorphonuclear leukocytes, monocytes and endothelial cells, causing inflammatory responses. Nickel complexes in the form of arsenides and sulfides are known carcinogens and mutagens effecting DNA damages.⁵ In view of the probable health hazards of nickel leach from bio-materials, its topographic correction has tremendous importance for safe orthodontic practice.

Investigations into the shape memory and super elasticity properties of surface modified NiTi wires are so far, very rare. In an exclusive study, using differential scanning calorimetry and X-ray diffraction on a surface modified NiTi with certain oxides, no differences in these features were observed.²⁸ This does not mean that all the surface modified NiTi products currently available have their requisite physical properties. It follows that experimental procedures for the correction of surface roughness of NiTi wires should not merely focus on reducing RMS values or surface roughness but should give due recognition for its physical properties like shape memory and super elasticity.

The current study proved that all surface modified NiTi groups showed considerable reduction in surface roughness compared with control. RMS values showed the following order: Group I; conventional NiTi (578.56 nm) > Group V; Teflon (365.33 nm) > Group III; nitride (301.51 nm) > Group VI (i); rhodium (290.64 nm) > Group VI (ii); silver (252.22 nm) > Group IV; titanium (229.51 nm) > Group II; resin (158.60 nm). Mean values of study groups differed significantly from the control in the analysis of variance (One-way ANOVA). The groups differed significantly from each other too, in the post hoc Duncan's multiple range (DMR) test.

From the foregoing, it is evident that surface roughness is a key property of NiTi arch wires, though certain aspects of relations between RMS values versus friction and corrosion still await clarifications.^{19,21,22} Further, role of the rough surface of NiTi in attracting oral plaque, biofilm organization and nickel leach have important clinical implications.⁵ The study explicitly brought out the defects of esthetic; resin/Teflon and nitride surfaces over NiTi. At the same time, it showed the correction of surface roughness achieved with metals. It thus stressed the need for having appropriate quality control in manufacturing surface modified NiTi wires. Since these procedures most likely entail high temperature and pressure applications on NiTi wires, its effects on shape memory and super elasticity are also to be closely scrutinized for ensuring optimum clinical results. For all these, surface roughness and RMS values would be a reckonable entity and a crucial assessment factor in NiTi arch wire research.

Inferences in the current study were based on the characterization tests done on 'as- received' samples. The efficacy of coatings and alterations in surface roughness values can be better understood, if the samples are retrieved after clinical use and subjected to a similar set of scrutiny. Future investigations based on clinically used samples would therefore be appropriate. Notwithstanding that, the results give clinicians firsthand information on topographic features of NiTi wires with surface coatings. It certainly adds on to the clinical knowhow and offers an opportunity to practice evidence based orthodontics with these new wires.

Conflict of interest

All authors have none to declare.

Acknowledgement

This paper is based on Armed Forces Medical Research Committee Project No 4232/2011 granted by the office of the Directorate General Armed Forces Medical Services and Defence Research Development Organization, Government of India. Dr Parvatha Varthini, Dr Sole and Dr Vanitha Kumari, Scientists at Indira Gandhi Centre for Atomic Research (IGCAR), Department of Atomic Energy (DAE), Kalpakkam, Tamil Nadu.

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Fig. E1 – (b) Group II, (c) Group III, (d) Group IV, (e) Group V, (f) Group VI (i) and (g) Group VI (ii).

Fig. E2 – (b) Group II, (c) Group III, (d) Group IV, (e) Group V, (f) Group VI (i) and (g) Group VI (ii).

Fig. E3 – (b) Group II, (c) Group III, (d) Group IV, (e) Group V, (f) Group VI (i) and (g) Group VI (ii).

Fig. E4 – (b) Group II, (c) Group III, (d) Group IV, (e) Group V, (f) Group VI (i) and (g) Group VI (ii).

Fig. E5 – (b) Group II, (c) Group III, (d) Group IV, (e) Group V, (f) Group VI (i) and (g) Group VI (ii).